Nucleation and growth of barium sulfate ($BaSO_4$) and calcium carbonate ($CaCO_3$) nanoparticles in aqueous solutions

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Relevancy of the Project

In Earth Sciences and Geoengineering, knowledge on crystal nucleation mechanisms is crucial to:

- quantify fluxes in biogeochemical cycles
- unravel the timing and rate of different geological processes
- unravel the physical and chemical conditions during crystal formation and prevent **scaling**
- evaluate crystal origin and quality and use that as a proxy for paleo-environmental conditions
- optimize crystal formation for subsurface remediation, stabilization and CO_2 sequestration

Figure 1: $BaSO_4$ scaling of geothermal energy, oil and gas pipelines leads to high repair and replacement costs [2].

Figure 2: Importance of $CaCO_3$ scale formation in drinking water industries as it is a nuisance in industrial and household appliances [3].

Pilot Study: $CaCO_3$ nucleation and growth

Methods

Cross-Polarized Light in Optical Light Microscopy (XPL-OLM)

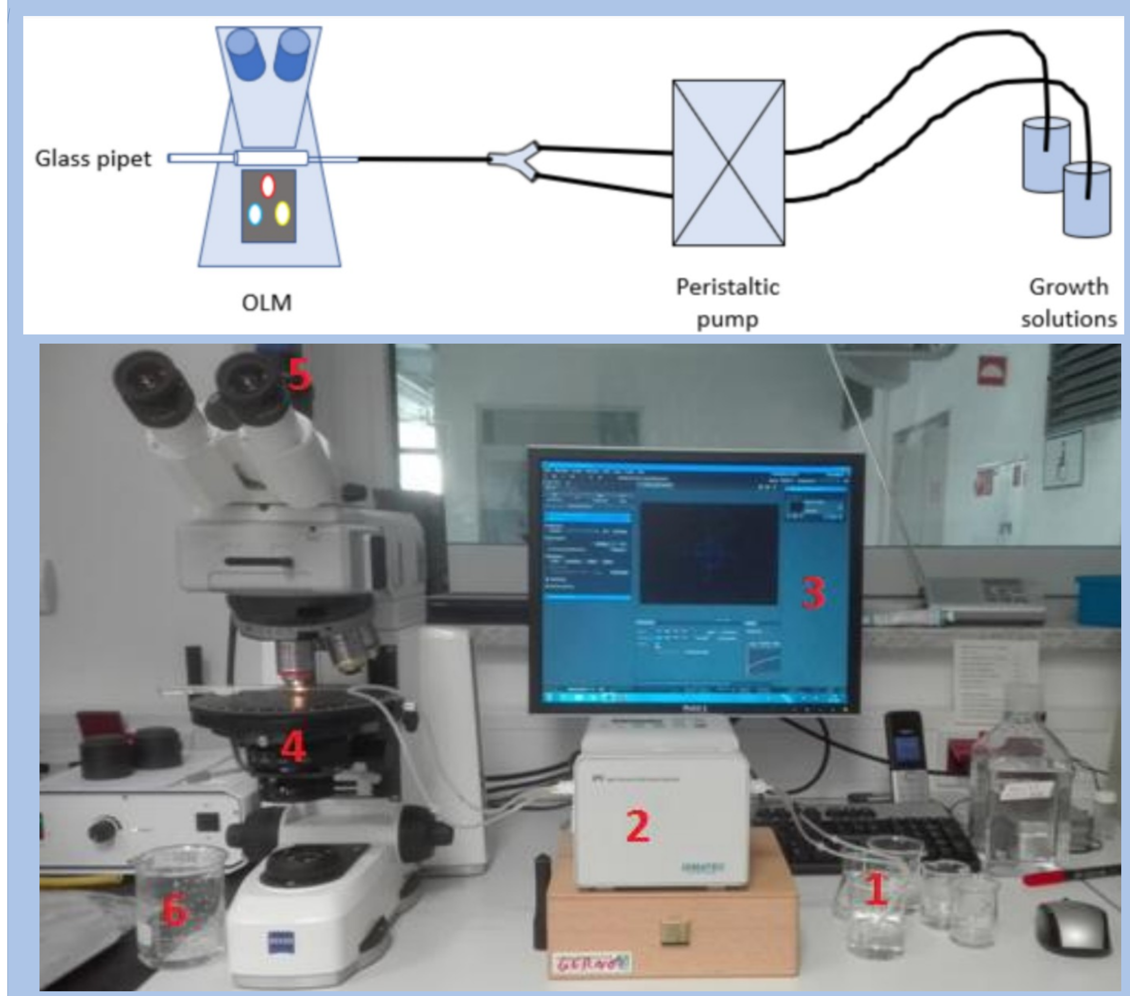


Figure 3: Experimental set-up during OLM-XPL experiments. The growth solutions (1); Peristaltic pump (2); Zen Lite software for recording & imaging (3); Optical light microscope (4); Axiocam attached to microscope (5); Beaker containing outflow solutions (6) [1].

Dynamic Light Scattering (DLS)

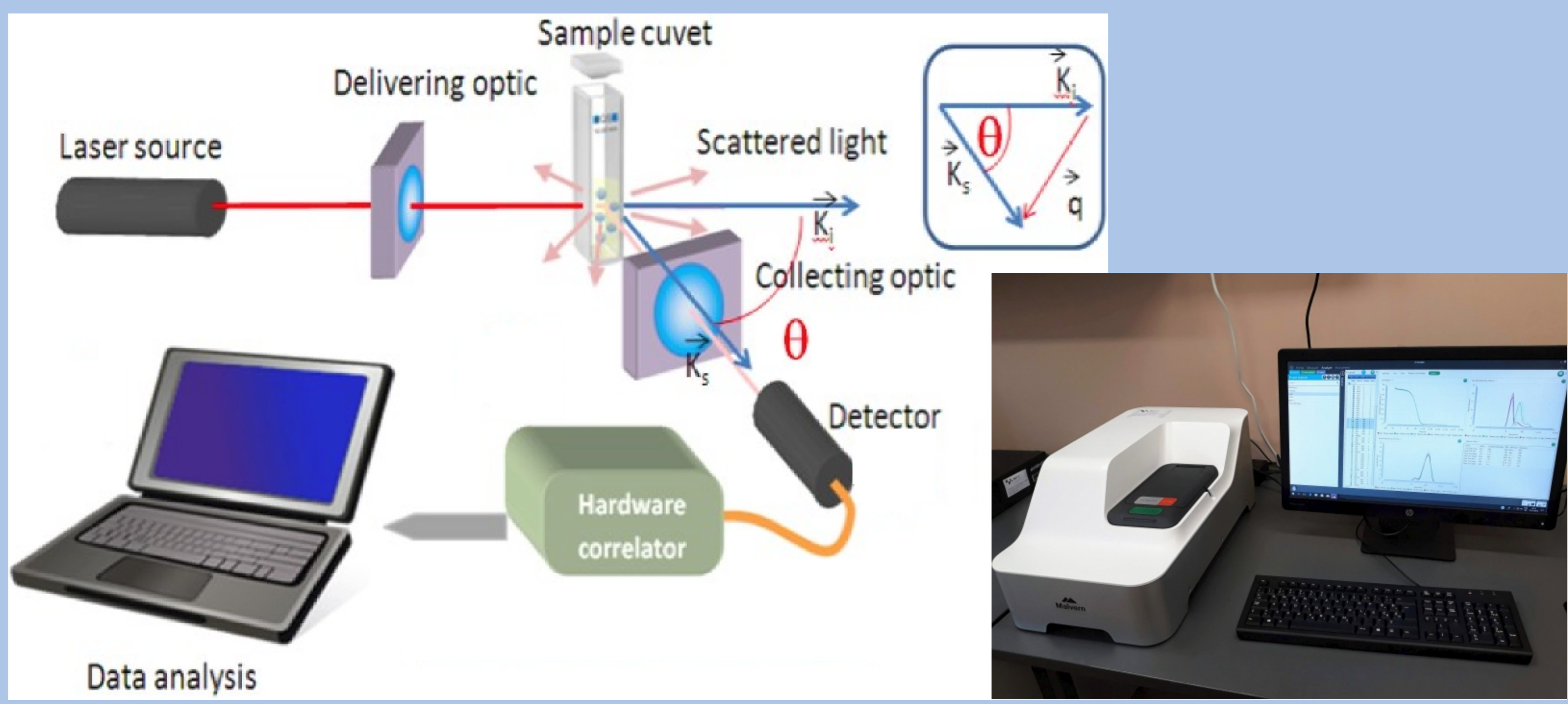


Figure 4: DLS makes use of Brownian motion of nanoparticles in a solvent in order to measure their size distribution. Launching a laser into the particles and looking at the scattering light in a specific direction allows to analyze the nanoparticle's size distribution [7].

Results

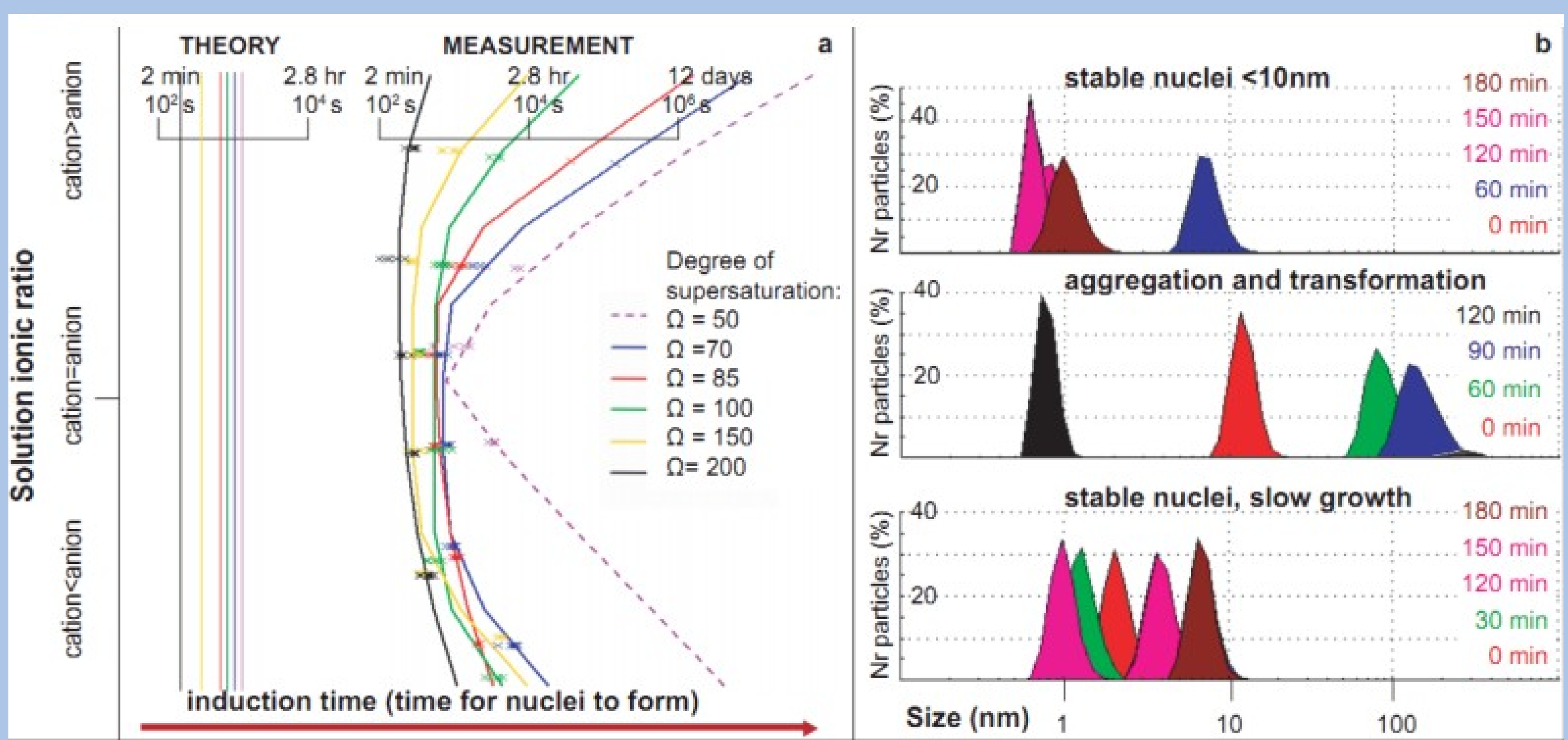


Figure 5: Besides pH, ionic strength and the supersaturation degree (Ω), the ionic ratio affects the timing of nucleation (a) and how the newly formed particles grow at $Ca:CO_3$ of ~0.01, 1.0, 100 (b). Induction time measurements were obtained by Cross-Polarized Light Optical Microscopy (XPL-OLM) and the time represents nucleation and subsequent growth up to 20 µm (a). DLS (detection limit ± 0.3 nm) was used to investigate the growth of the crystals (b) [1].

Conclusions

- $CaCO_3$ nanoparticles nucleate and grow most rapidly at ideal $Ca:CO_3$ of 1
- In non-stoichiometric solutions, particle sizes remain < 10 nm up to a few hours
- The nucleation pathway is influenced by the ionic ratio of the solution

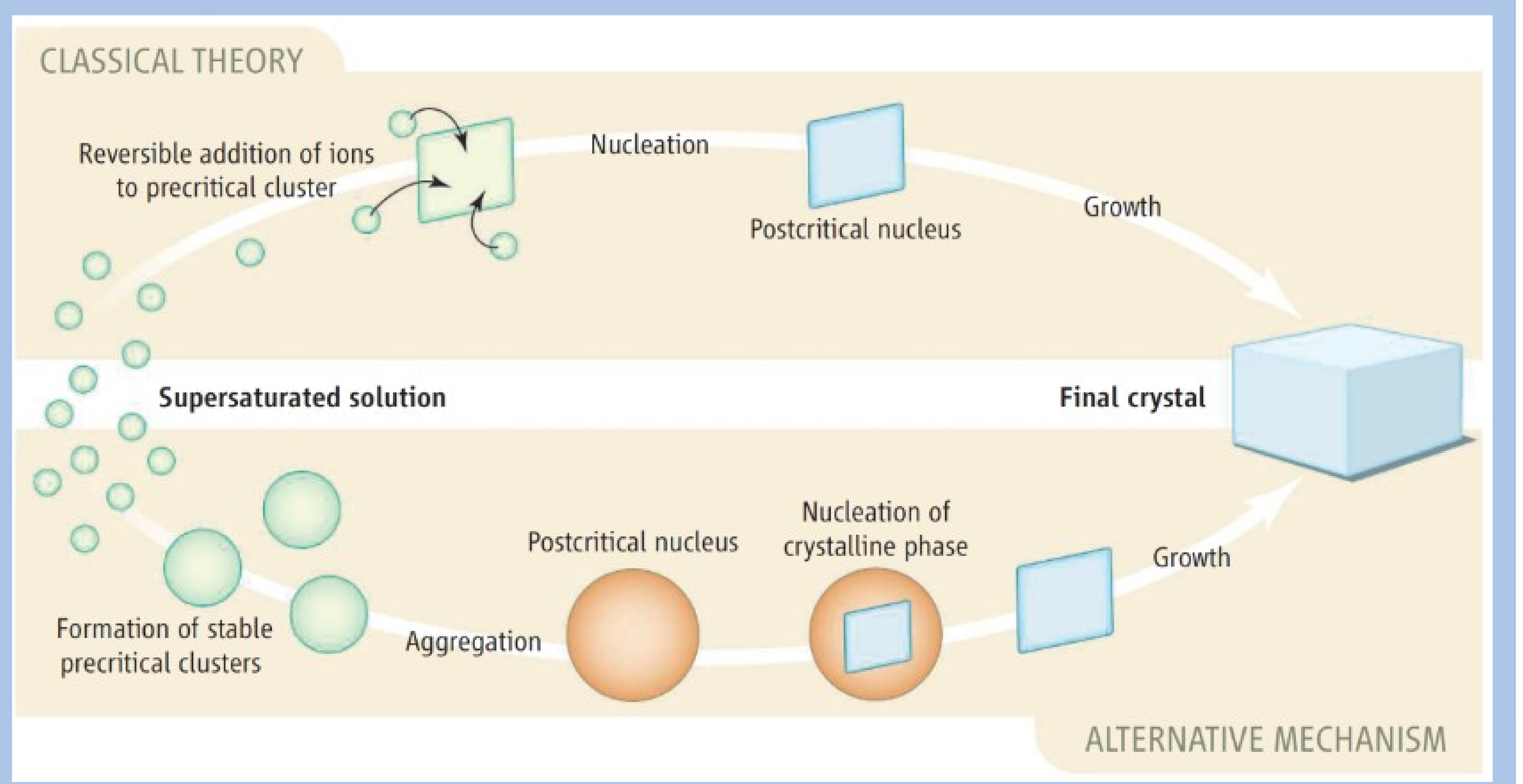


Figure 6: two well known nucleation pathways; The classical nucleation pathway assuming ion-by-ion cluster formation and subsequent growth (upper) and the aggregation pathway, forming large postcritical nucleii from precluster-sized particles, followed by nucleation and subsequent growth (lower) [4].

Research Questions and Approach during Project

1) Does nucleation depend on the ionic ratio?
   → Measure timing and rate of nucleation vs. ionic ration (DLS)
2) Are nuclei formed at high/low ionic ratio charged?
   → Measure nuclei charge vs. ionic ratio (Electrophoretic Light Scattering; ELS)
3) Does nucleus charge determine the critical nucleus size?
   → Measure nuclei size distributions during nucleation at different ionic ratio (DLS)
4) Does nucleus charge determine the ripening pathway?
   → Follow ripening of nuclei with time (morphology, crystallinity, transformation using **liquid-cell** and **cryo-TEM**)

$CaCO_3$

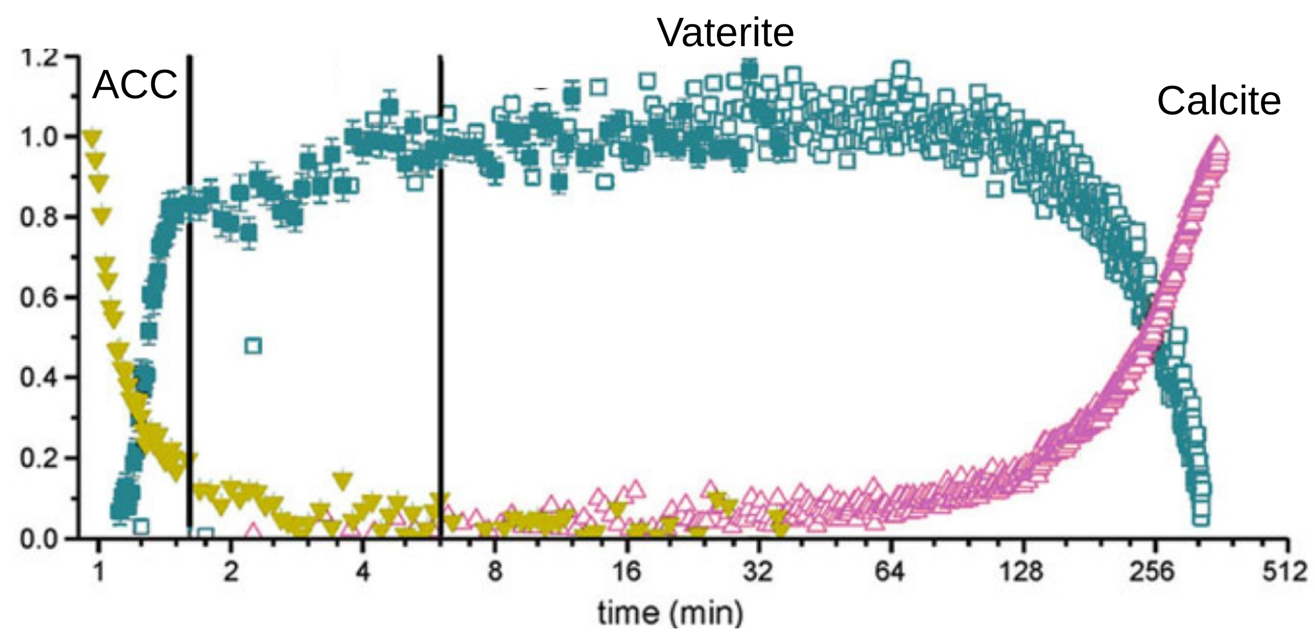
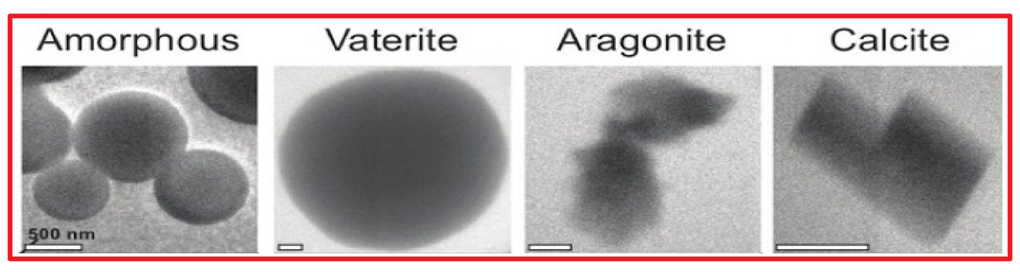


Figure 7: Schematic representation of the reaction progress for the crystallization reaction in a pure system. It is a multistage crystallization pathway going from Amorphous Calcium Carbonate (ACC) → Vaterite → Calcite [5].

Ultimate Goal of Project

- Derive new expressions to include nucleus charge in the nucleation thermodynamics, kinetics and ripening, by combining new relations with nucleation and colloid theories
- To apply the new theory on natural settings where expected crystal formation does not occur



TEM

Figure 8: in situ TEM images of ACC, vaterite, aragonite and calcite [6].

References

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